

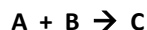
**Using Graphical Analysis to Determine Reaction Order**  
**IB HL Chemistry**  
**23 Marks Total**

*This activity was created by T. A. Hennard, a former Chemistry teacher at ECA. The assignment was created specifically for Verneirs Graphical Analysis Program but we will attempt to use a combination of Autograph, Logger Pro, and Excel to complete the tasks.*

**Background Information:**

Everyone knows that some chemical reactions occur quite fast while others are quite slow. The description and mathematical manipulation of these processes is known as kinetics. Almost all chemical reactions are multistep processes, and in every chemical reaction there will be one step that is the slowest, that slows the rest of the reaction down to its speed. This is known as the *rate determining step*. Chemical kinetics is almost entirely concerned with this rate determining step since any effort to measure the rate of a reaction will inevitably give you the rate of the rate limiting step.

In order to understand this activity you must know a little about how reaction rates are communicated. For a reaction of A and B reacting to give C:

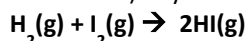


we write the mathematical equation describing the reaction rate as follows:

$$\text{Rate} = k [A]^m [B]^n$$

where [A] and [B] are the concentrations of A and B, respectively, and m and n are values to which A and B are raised. m and n do not have to be integers, though they normally are, and their value is **always** determined by experiment. There is no way to determine beforehand the value of m or n—it is an experimental value. The rate is always given in speed units (such as moles/second) and k is a constant that changes only with temperature and is independent of all other factors.

An example might be helpful. If you react hydrogen gas and iodine together you will create hydrogen iodide. Since iodine is colored and hydrogen and hydrogen iodide are not, you can measure the speed of the reaction by how quickly the iodine color disappears (though this is more difficult than it would at first seem). If you do a series of studies on the reaction:



you find that you can double the reaction rate by doubling the hydrogen concentration. You can do the same thing by doubling the iodine. The rate equation for the reaction is therefore:

$$\text{Rate} = k [H_2] [I_2]$$

and the values to which the concentrations of hydrogen and iodine are raised are both 1. This value is important for several reasons, but most importantly it allows us to assign a *reaction order* to that reactant. In this case we say, “The reaction is first order with respect to both hydrogen and iodine,” since the value to which both were raised is 1. A reaction may be zero order with respect to a reactant or catalyst. In the reaction of bromine with methanoic acid:

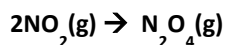


the reaction is catalyzed by the addition of a strong acid. No matter how much or how little strong acid one puts in the reaction, the rate does not change at all! It has no effect. That means that the rate with respect to the strong acid would be:

$$\text{Rate} = k [\text{acid}]^0$$

Since anything raised to the zero power is 1, that means

Rate = k, or a constant. The rate doesn’t change with acid and we say, “The reaction is zero order with respect to acid.” In the reaction of nitrogen dioxide to form dinitrogen tetroxide:



the rate equation turns out to be:

$$\text{Rate} = k [NO_2]^2$$

meaning that if you double the nitrogen dioxide, you quadruple the rate! We say, “The reaction is second order with respect to nitrogen dioxide.” It’s worth repeating that, though the coefficient of 2 in the equation and the power of 2 in the rate equation are undoubtedly related, you can’t simply say that it will be second order by looking at the balanced chemical equation. It can only be determined by experiment.

The mathematics behind this type of kinetics is relatively straightforward. The first thing that you do when manipulating kinetics data is to create a graph of concentration of the reactant that you are looking at. If the reaction is zero order then the rate does not depend on the concentration of this species and the graph will be a straight line. If the reaction is first or second order, then the rate will fall off as the concentration of the species falls and therefore the graph will show a curve. It can be quite difficult to determine by eye whether this curve belongs to a first or second order reaction.

Fortunately there are ways of determining whether it is first or second order. The simplest way is to take advantage of some mathematical truisms of kinetics:

- The graph of concentration vs. time is straight for a zero order reaction.
- The graph of  $\ln[\text{concentration}]$  vs. time is straight for a first order reaction. I see know need to go into the mathematics behind this. It is irrelevant to the syllabus and we simply use it for a test.
- The graph of  $1/\text{concentration}$  vs. time is straight for a second order reaction.

Another way is to manipulate the data to give you reaction rates instead of concentrations, then graph those. For a first or second order reaction, a graph of concentration vs. time will give a curve. You can see from the curve that the reaction rate is falling throughout the reaction. You can determine the reaction rate at any particular moment by drawing a tangent to the curve at that point, then finding the slope of the tangent line. Since slope is  $y/x$ , the resulting quantity will be concentration/time—a speed or rate unit! Then all you must do is determine the rate at several points on the curve and graph them—rate vs. concentration. If the curve of rate vs. concentration is a straight line, then the reaction is first order. If it still isn't straight, then perhaps it's second order. In that case try graphing the rate vs. the concentration raised to the second power. If that is straight, then the reaction is second order.

All in all, I prefer to use the second method with students because it forces them to use the original data to determine rates and gives some feeling for how such quantities are generated. The first method is a bit “magical” to them, I've discovered.

In order to use the second method, one must have a nice curve to find tangents to. In order to generate such a curve, you need to fit a model to the data. A first order reaction will be modeled nicely by an exponential curve and a second by a quadratic. The use of the graphing program makes it easy to try different curves then calculate tangent slopes and manipulate and graph the data without difficulty.

#### Directions for the Activity:

In this activity we will explore three sets of reaction data. The first set will be a practice set in which you will discover some of the tools and techniques of kinetics. The other two will be for you to play with yourself.

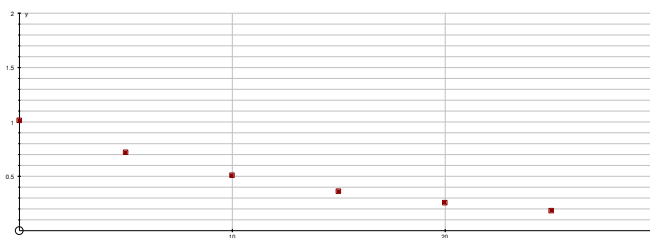
The first data set is taken from a hypothetical reaction in which the concentration of reactant A decreases with time according to the following data:

Time (sec)	Conc (mol/L)
0	1.012
5	0.7189
10	0.511
15	0.3632
20	0.2581
25	0.1835
30	0.1304

Using Graphical Analysis, we will explore this data set and determine whether this reaction is zero, first or second order in A.

#### Procedure:

- Enter the data into the X and Y columns of the GA program and change the label and units (by double-clicking the X and Y) to the ones shown in the data set. You should now have a curve.



- Use what you know about concentration vs. time graphs of reactions. *Is this a zero order reaction? First? Second? Briefly explain why you can either reject or possibly accept each of these possibilities. **First or second, because it's not straight, further manipulation would show which, but for now we cannot tell the difference.***
- If you are unsure of what the order is, one method is to do a graph of rate vs. concentration. The rate of a reaction is a measure of how fast it is going. *Is the rate of this reaction increasing or decreasing as it continues? **Decreasing*** One method of measuring the rate at any particular point is to find the tangent line to that point then determine the slope of that line. Since slope is  $y/x$ , this will come out as concentration/second, which is a rate unit. In order to do this, however, it's necessary to have a nice smooth curve instead of discrete points like we've got. To do this you must fit a “model” curve

to the data. For example, if the points lay along a line we would say that a linear model was appropriate. The three possible models for zero, first and second order reaction data are linear, exponential and quadratic. We can try each of them very quickly using the GA program.

4. Go to "Analyze" and click on "Automatic Curve Fit." Try the linear model by double clicking on "Linear." *Does that look like a very good fit for this curve?* **No**, Cancel and try "Exponential." *Does that look like a good fit?* **Yes**. Cancel and try "Quadratic." *Does that look like a good fit?* **Yes**. Remember that the value "Mean Squ. Err" (mean square error) in the curve fitting dialog box is a measure of the goodness of fit. The smaller the mean square error, the better the fit. Now choose the best model and click "OK-Keep Fit."
  5. Now you can determine the rate at all of the points along the line, enter it into your spreadsheet and determine the order. Go to "Data," choose "New Column" and "Manually-Entered." Label it Rate and write Slope for units. Now go to "Analyze" and choose "Tangent Line." This will give you the slope at any of the points that aim your cursor at. Take the slope in black (that's the one from the curve you fit to the data), change the sign to positive (to make the graph look right) and enter them into your new column.
  6. Now you can create a graph of rate vs. concentration and check to see if it's first order. Double click on the y-axis label on the graph and choose Rate and un-choose Concentration. Double click on the x-axis label on the graph and choose Concentration. *Is this a straight line graph? Then it's first order.* Now it may not look like a straight line at first, but fit a linear curve to it. *Doesn't the small value of the mean square error indicate it's a straight line?*
  7. Now create another column, but this time make it "Calculated." Call the label "Squared" and leave the unit blank. Into "New Column Formula" enter the following formula: "Concentration"^2 (use the "Columns" button to enter the "Concentration" function). Hit OK and the new column will fill with the square of the concentrations. Change the graph so that it is Rate vs. Concentration Squared. If it is a straight line, then the reaction is second order. *Is the reaction second order?*
  8. So now that you've discovered one way of determining whether a reaction is first or second order, let's try the other. Here are a couple of truisms about first and second order reactions:
    - a. If a graph of  $\ln(\text{concentration})$  vs. time is straight, the reaction is first order.
    - b. If a graph is  $1/\text{concentration}$  vs. time is straight, the reaction is second order.
- So, create another calculated column and enter the formula of  $\ln(\text{concentration})$ , then change the graph so that the y-axis is  $\ln(\text{concentration})$  and the x-axis is time. *Is it a straight line?* Then it's first order.
9. Just for practice, create another calculated column that is  $1/\text{concentration}$  and graph it vs. time. *Is it a straight line?* Then it's not a second order reaction.
  10. Now you've got all the tools that you need to determine zero, first and second order reactions.
    - a. Graphs of concentration vs. time. If it's straight it's zero.
    - b. Graphs of rate vs. concentration. If it's straight, it's first.
    - c. If a graph of rate vs.  $(\text{concentration})^2$  is straight, it's second.
    - d. Graphs of  $\ln(\text{concentration})$  vs. time. If it's straight, it's first.
    - e. Graphs of  $1/\text{concentration}$  vs. time. If it's straight, it's second.
  11. Now we get to the fun part, playing with data for yourself. The following data was taken from the reaction of bromine and methanoic acid:



The first is data on bromine concentration vs. time: (note: conc = 0.006 when t = 120)

Time(seconds)	Bromine Conc(mol/L)
0	0.01
30	0.009
60	0.008
90	0.007
120	0.007
180	0.005
240	0.004
360	0.003
480	0.002
600	0.001

The second is data on the same reaction, but it's methanoic acid vs. time:

Time(seconds)	Methanoic Conc(mol/L)
0	0.01
30	0.009
60	0.008
90	0.007
120	0.006
180	0.004
240	0.002

Your mission is simple--determine the order of the reactions. You're required to have the following things:

1. A concentration vs. time graph for each data set.
2. Two pieces of evidence (graphs) to support your claim of each data set as representing zero, first or second order reactions. At least one graph must be of the rate vs. concentration or concentration<sup>2</sup> type. This is to ensure that you know how to take rates off of concentration graphs using slopes of tangent lines.
3. An explanation written for each piece of evidence written so that even an idiot (like your chemistry teacher) will be convinced that the reaction is the order that you say it is.

**Assessment:**

The activity will be scored in the following manner:

1. Completion of the preliminary activity. **(5 marks)**
2. A concentration vs. time graph for each data set. **(1 mark each--2 total)**
3. Two pieces of evidence (graphs) to support your claim of each data set as representing zero, first or second order reactions. At least one graph must be of the rate vs. concentration or (concentration)<sup>2</sup> type. This is to ensure that you know how to take rates off of concentration graphs using slopes of tangent lines. **(2 points for each graph--8 total)**
4. An explanation written for each piece of evidence written so that even an idiot (like your chemistry teacher) will be convinced that the reaction is the order that you say it is. **(2 points for each explanation--8 total)**